

989,005



PATENT SPECIFICATION

DRAWINGS ATTACHED

989.005

Date of Application and filing Complete Specification: Jan. 11, 1962.

No. 1052/62.

Application made in United States of America (No. 82053) on Jan. 11, 1961.

Application made in United States of America (No. 162,320) on Dec. 22, 1961.

Complete Specification Published: April 14, 1965.

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Index at acceptance:—C1 J(1, 2, 4, 5, 7, 9, 11, 14, 17, 18, 19, 20, 21, 22, 24, 25, 28, 31, 34, 35); B5 N(2F, 2M1, 2X, 13, 16A); C1 A(13, N4B, N10A, N11, N13A, N16, N22, N33, N34, N40, N47A, N48A, N52); C7 A(8A1, 8A2, 8B, 8D, 8E, 8G, 8H, 8K, 8M, 8Q, 8R, 8T, 8U, 8W, 8Y, 8Z1, 8Z2, 8Z3, 8Z4, 8Z5, 8Z8, 8Z9, 8Z12, 11, 12, 13, 14, 15A, 15B, 15C, 17, 21, X)

Int. Cl.:—C 04 b // B 29 d, C 01 f, g, C 22 c

COMPLETE SPECIFICATION

Refractory Product and Process for its Manufacture

AMENDMENT

SPECIFICATION NO. 989,005

Page 1, Heading -- Delete "Application made in United States of America (No. 162320) on Dec. 22, 1961"

THE PATENT OFFICE,
30th June 1965

D 39846-1

10 20% to 90%, and comprising a rigid aggregate
of metal oxide shapes having at least one
dimension of from 0.5 to 125 mils, the oxide
shape being either (A) the oxide formed by
the *in situ* oxidation with gaseous oxygen of
20 aluminium, beryllium, calcium, chromium,
niobium, copper hafnium, iron, magnesium,
nickel, silicon, tantalum, thorium, titanium, or
zirconium or an alloy in which one of said
metals constitutes the predominant component
25 or (B) a composite of (A) and the oxide of a
different metal than that recited in (A) which
metal is an alkali metal, an alkaline earth
metal, vanadium, chromium, molybdenum,
tungsten, copper, silver, zinc, antimony or bis-
30 muth, the composite containing from 4.6% to
99.95% by weight of metal oxide formed
in situ and from 0.02% to 20% of the oxide
of the said different metal, the crystalline re-
fractory being further characterised by a re-
35 sidual metal content from the formation of (A)
of no greater than 85% and, when present,
no more than 95% of a filler refractory as here-
inafter defined, the said filler being particulate,
crystalline and substantially unfused.
40 This product is formed, according to the

baenum, tungsten, copper, silver, zinc, anti-
mony or bismuth or (III) trialkyl tin oxide or
lead silicate and (C) from 0% to 95% of a
particulate, crystalline filler refractory, the
contacted mass of (A), (B) and (C) having a
porosity, after removal of volatile materials, of
60 at least 20%, and thereafter oxidising the
metal in the contacted mass with gaseous
oxygen at a temperature of at least 400°C. and,
if the filler refractory is present, below that
at which the filler refractory fuses for a period
65 of time sufficient to give rise to a weight gain
of at least 10% based on the weight of the
metal employed.

A number of expressions used in the present
specification will now be defined. By a
70 "crystalline refractory" is meant that the oxide
of the structure will diffract X-rays in a
discrete manner, i.e. it is a non-glassy material.
Generally, it is preferred that no more than
a minor amount of such glassy material, i.e.
75 no more than about 10% by weight be pre-
sent in the final structure. By "particulate"
is meant that the material is of a sufficiently
small particle size that it will pass an 8-mesh
screen. By a "filler refractory" is meant a
80

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Int. Cl.:—C 04 b // B 29 d, C 01 f, g, C 22 c

COMPLETE SPECIFICATION

Refractory Product and Process for its Manufacture

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a refractory product and a process for its production.

The present invention provides a crystalline refractory characterised by a porosity of from 20% to 90%, and comprising a rigid aggregate of metal oxide shapes having at least one dimension of from 0.5 to 125 mils, the oxide shape being either (A) the oxide formed by the *in situ* oxidation with gaseous oxygen of aluminium, beryllium, calcium, chromium, niobium, copper hafnium, iron, magnesium, nickel, silicon, tantalum, thorium, titanium, or zirconium or an alloy in which one of said metals constitutes the predominant component or (B) a composite of (A) and the oxide of a different metal than that recited in (A) which metal is an alkali metal, an alkaline earth metal, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony or bismuth, the composite containing from 4.6% to 99.95% by weight of metal oxide formed *in situ* and from 0.02% to 20% of the oxide of the said different metal, the crystalline refractory being further characterised by a residual metal content from the formation of (A) of no greater than 85% and, when present, no more than 95% of a filler refractory as hereinafter defined, the said filler being particulate, crystalline and substantially unfused.

This product is formed, according to the

invention, by a process which comprises intimately contacting the surfaces of (A) from 4% to 99.98% by weight of particles of aluminium, beryllium, calcium, chromium, niobium, copper, hafnium, iron, magnesium, nickel, silicon, tantalum, thorium, titanium or zirconium or an alloy in which one of said metals constitutes the predominant component with (B) from 0.02% to 20% by weight of a fluxing agent which is either (I) an oxide of a metal other than those recited in (A) or (II) a precursor of the oxides of (I), the oxides of (I) being of an alkali metal, an alkaline earth metal, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony or bismuth or (III) trialkyl tin oxide or lead silicate and (C) from 0% to 95% of a particulate, crystalline filler refractory, the contacted mass of (A), (B) and (C) having a porosity, after removal of volatile materials, of at least 20%, and thereafter oxidising the metal in the contacted mass with gaseous oxygen at a temperature of at least 400°C. and, if the filler refractory is present, below that at which the filler refractory fuses for a period of time sufficient to give rise to a weight gain of at least 10% based on the weight of the metal employed.

A number of expressions used in the present specification will now be defined. By a "crystalline refractory" is meant that the oxide of the structure will diffract X-rays in a discrete manner, i.e. it is a non-glassy material. Generally, it is preferred that no more than a minor amount of such glassy material, i.e. no more than about 10% by weight be present in the final structure. By "particulate" is meant that the material is of a sufficiently small particle size that it will pass an 8-mesh screen. By a "filler refractory" is meant a

melt resistant carbide, nitride, boride or oxide as more particularly identified below which is present in either the green or the fired structure and is not oxidisable by gaseous oxygen under the conditions of the firing operation. The term "unfused" is used in its usual connotation of "not blended as if melted together". The term "composite" is intended to include mixtures, compounds and solid solutions. "Oxidation with gaseous oxygen" means that the oxygen supplied to the metal is derived from the surrounding atmosphere rather than from another oxide as in an oxidation-reduction (thermite) type of reaction. Oxidation by gaseous oxygen is characterised by a weight gain during firing due to the addition of oxygen to the structure which weight gain is not experienced in the thermite reaction where the source of oxygen is self-contained in the solids of the green structure. "Gaseous oxygen" includes air, pure oxygen and oxygen diluted with any gas substantially inert in the reaction. Porosity of the green structure is essential to permit penetration of the oxygen-bearing gases into its interior. By a "precursor of the oxide" is meant a material which under the firing conditions produces the oxide. Throughout this description, all parts and percentages are calculated on a weight basis.

In order that the invention may be more fully understood, reference will be made hereinafter to the accompanying drawings in which:—

Figure I is a photomicrograph at a magnification of about four times of a ground surface of a structure of the present invention, more particularly identified in Example 1;

Figure II is a pen and ink representation of a fragment of an edge view of a honeycomb structure of the present invention, more particularly identified in Example 2;

Figure III is a photomicrograph at a magnification of about four times of the surface of a structure of the present invention, more particularly identified in Example 4;

Figure IV is a photomicrograph at a magnification of about 270 times of a section of the brick of Example 10c;

Figure V is a photomicrograph at a magnification of about 20 times of a section of a structure prepared substantially as that identified in Example 11;

Figure VI is a diagrammatic representation of one type of product formed in accordance with the present invention, more particularly described below;

Figure VII is a photomicrograph at a magnification of about 150 times of a section of a structure prepared substantially as that identified in Example 15c; and

Figure VIII is a diagrammatic representation of a second type of product formed in accordance with the present invention, more particularly identified below.

In any refractory formed in accordance

with the present invention, the internal structure has been observed to depend largely on the percentage by weight of unoxidised metal in the green structure and the morphology of the metal. Generally two extreme forms of internal arrangement are possible with a wide range of intermediate and mixed structures between these extremes. The two extreme forms as described in greater detail below are those characterised by a continuous "integral skeleton" and those having no such skeleton. Those having a continuous integral skeleton are preferred, due to their very high thermal shock resistance, high flexural strength and high abrasion resistance.

Continuous Integral Skeleton

When large granular and non-granular metal shapes are employed, e.g. funicular, acicular or pellicular, which may be derived from structures such as a filament, continuous fibre, staple, yarn, hair, floc, sliver, shred, shaving, splinter, paring, film, foil, or ribbon, at a percentage by weight of at least about 20% of the total green composition, a substantially continuous integral skeleton of high density and substantially homogeneous composition of the oxide of the metal used is formed. In forming this structure it is preferred that at least 0.1% by weight of the fluxing agent be employed, that no more than 80% of particulate, crystalline filler refractory be present and that the porosity of the green structure be at least 25% after drying to remove volatile materials. Preferably also the non-granular metallic shapes have one dimension of from 0.5 to 125 mils, a second dimension of at least 10 mils and a third dimension of at least 0.5 mil, the second and third dimensions being at least equal to the first dimension. The green structure is preferably heated to a temperature of at least about 700°C. in an oxygen atmosphere for a period of time sufficient to cause oxidation of at least sufficient of the metal to form the substantially continuous integral skeleton. This generally is observed to occur when sufficient oxygen has been added to the structure to increase the weight of the originally metallic component of the green structure by at least 10%.

The structure formed from aluminium is represented diagrammatically in Figure VI. As will be seen from the figure, voids 1, corresponding substantially in shape to the shape of the original metal particles, are formed. The spaces between the voids, which correspond roughly to the spaces between the metal particles in the green structure, have become substantially filled with metallic oxide formed *in situ* 2. Pores 3, which are spaces between the metal particles in the green structure not filled by metallic oxide formed *in situ*, also exist in the final structure. Filler refractory 4 is dispersed in oxide 2. At times an unoxidised fragment of aluminium 5 can be found, par-

ticularly when the oxidation in the firing stage
 is not complete. Similar structures are shown
 are shown photographically at different magni-
 fications in Figures IV and V. The various
 5 parts are labelled in Figures IV to correspond
 to those identified in Figure VI discussed
 above. In Figure IV the voids contain plastic
 filler due to the technique employed in polish-
 ing samples for photographic purposes at this
 10 magnification. Optical properties of the
 materials create a well defined optical bound-
 ary 6 between the plastic and the solids of
 the refractory body. While applicant does
 not wish to be bound by an particular theory,
 15 it is believed that mutual molecular intra-
 distribution of *in situ* formed metal oxides
 results to form the continuum during the
 formation and expansion of the *in situ* formed
 oxide. The final structure is characterised by
 20 a porosity of between 25% and 90%. The
 metal preferred in forming these structures is
 aluminium. When formed from aluminium,
 the continuous skeleton of these refractories is
 25 further characterised by a cellular structure in
 which the cells, voids or pores of the body
 have an average diameter of between 50 mic-
 rons and 500 microns. The grains have a
 density function (i.e. an average ratio of
 30 perimeter in contact with other grains to the
 total perimeter under consideration of from
 between 0.5 and 1.0. They are further charac-
 terised by an alumina content of from 32%
 to 100% by weight, a flexural strength at
 35 25°C. and 1550°C. (corrected to zero poro-
 sity) of at least about 500 pounds per square
 inch, a thermal shock resistance such that the
 object is not cracked or eroded upon sudden
 exposure of the room temperature structure to
 40 a 1500°C. flame, and abrasion resistance.
 Structures of this type are exemplified in
 Examples 1 to 14.

"No Skeleton" Products

Particularly when small granular metal
 shapes are employed at a concentration in the
 45 green structure of less than 20% by weight of
 the green structure and in the presence of
 from 80% to about 95% by weight based on
 the green structure of particulate crystalline
 filler refractories (particle size such that they
 50 will pass an 8-mesh and preferably a 20-mesh
 screen), a refractory is formed which does not
 possess the "integral skelton" described above.
 In forming this structure, it is preferred that
 from 0.05% to 5.0% by weight based on the
 55 green structure of fluxing agent from the class
 consisting of the oxides of alkali metals, the
 hydroxides of alkali metals, and precursors of
 the oxides of the alkali metals be employed.
 Preferably the metallic shapes are of such
 60 dimension that the ratio of surface area to
 volume is between about 100 mm.⁻¹ and about
 7 mm.⁻¹. The green structure is preferably
 heated to a temperature between 650°C. and
 1050°C. for a period of time sufficient to

cause oxidation of at least sufficient of the
 metal to cause bonding of the particulate
 refractory. Optionally this may be followed by
 a second heating between 1100°C. and 1600°C.
 for full firing. This structure is represented
 schematically in Figure VIII. As will be seen
 70 from the figure, in this embodiment the par-
 ticulate filler refractories 4 are bonded by the
 metallic oxide 2 resulting from the *in situ*
 oxidation of the metal originally present in the
 green structure. Pores 3 are also present in the
 75 structure. If the original metal is of sufficient
 particle size it will form voids 1 on oxidation.
 When *in situ* formed aluminium oxide is used
 to bond magnesium oxide as a filler, oxide
 2 is at least in part a spinel due to reaction
 with the filler. The final refractory product is
 characterised by a porosity of between 20 and
 80 70%. The metal preferred in forming these
 structures is aluminium. When formed from
 aluminium the structure is further characterised
 by grain size of the *in situ* formed oxide of
 85 less than about 5 microns, the said *in situ*
 formed oxide comprising from 9 to 45% by
 weight of the formed structure, the remaining
 structure being the unfused residue of the
 90 particulate filler refractory employed in mak-
 ing the green structure. Structures of this type
 are exemplified in Examples 15 and 16.

General Product Description

In addition to the refractories of two extreme
 95 internal forms described above, it is obvious,
 as stated previously, that a wide range of
 structures is possible, including both inter-
 mediate and mixed types of the two extremes.
 In any of the forms a minor amount of un-
 100 oxidised metal may remain in the final struc-
 ture. Alternatively, residual metal may be
 melted out of the refractory where porosity
 permits. In addition, after treatments may be
 used such as firing at high temperature to
 105 fuse filler refractories together where internal
 structure permits.

The form which the refractory is to take
 is readily shaped from the mass of metal
 110 particles whose oxide constitutes the final
 structure. Thus crucibles, cones, catalyst sup-
 ports, tube sections, motor casings, bearings,
 abrasion wheels, bricks, insulating panels and
 the like, can be readily fabricated. Laminates,
 115 particularly where corrugations permit access
 of an oxidation atmosphere between adjacent
 layers, may be readily formed into cellular
 type structures, having excellent insulation and
 mechanical properties.

Physical Tests

In the following examples porosities are
 120 calculated from the apparent density (weight
 of the body in air/mass volume of the body
 including opened and closed pores), and the
 density of the solid material as obtained by
 125 crushing the sample and determining the
 volume of the solids and their weight. The

latter measurement is conveniently made on an air comparison pycnometer. As an approximation, the porosity may be calculated from the apparent density and the calculated density of the solid material in a body of known composition. All sieve measurements are made with U.S. Sieve Series.

Flexural strength is measured according to ASTM Standard 1958, Part 4, page 670, Text No. C293—57T with the use of a span width of 1 to 4 inches.

For better comparison between properties, the flexural strengths are corrected for porosity of the sample by the expression

$$\frac{\text{flexural strength (as measured)} \times 100}{100 - \% \text{ porosity}}$$

Porosity actually causes a much greater decrease in strength than this correction implies.

The hot load subsidence is measured according to ASTM C16 schedule 7, modified to use a cylindrical sample $2\frac{1}{4}$ inch in diameter by 2 inches thick.

The abrasion resistance test is performed by pushing a $\frac{1}{2}$ inch by $\frac{1}{2}$ inch sample along a 6 inch hard bastard steel file by hand under a force of about 3 pounds for 8 strokes. The weight loss by abrasion is reported.

Grain size is determined by the following procedure: The sample is mounted by placing the sample covered with sealing wax in a cold oven and then raising the temperature to about 150°C. under vacuum. The sample is then rough polished using silicon carbide papers of 80, 120, 240, 400 and 600 grit in that order. The sample is then fine polished using Elgin

6 and 1 dymo diamond abrasive on rough and fine pellow lap on a convenient polishing wheel.

The wax is removed from the polished sample by melting most of it and burning the remainder in a Meker Burner Gas flame.

The sample is immersed in boiling concentrated phosphoric acid (H_3PO_4) for about 5 to 30 seconds after which it is rinsed in water, fired and examined under a Bausch and Lomb Research Metallograph. The sample is returned to the phosphoric acid bath for more etching for increasingly shorter etching exposure times.

The skeletons of the examples of this invention show very few visible grain boundaries after etching and examination under the metallograph at 750X magnification. This indicates a general grain size of less than 1 micron, i.e., 90—95% of the grains are less than 1 micron and 5 to 10% of the grains are between 1 and 5 microns in size. Examination of conventionally formed articles of dense polycrystalline alumina shows discrete grain boundaries after etching with an average grain size of 20 or more microns. This indicates the unique nature of the bond formed by the low temperature process of this invention.

Cell (or pore) size is determined by the lineal analysis of microstructure technique as discussed by W. D. Kingery in "Introduction to Ceramics", pages 412—417 (published by John Wiley and Sons, Inc., New York, 1960). The individual cells of products of this invention may have diameters varying from 1 to 2000 or 3000 microns depending upon the shape of the aluminium used in the process. However, the larger cells with a diameter of from 50 to 500 microns form the substantial portion of the total porosity.

$$\text{Density function} = \text{average} \left[\frac{\text{part of perimeter in contact with other grains}}{\text{total perimeter of grain under consideration}} \right]$$

Products of this invention show values of the above between 0.5 and 1.0 while products of the prior art have values of lower than 0.5.

The density function is determined by examining a photomicrograph of a polished section of the sample for each grain and averaging the results. Most products of this invention, as made, show no visible grain boundaries after etching and viewing at 750X magnification. In this event the value of the density function approaches an upper limit of 1.0. Grain growth can occur with prolonged heating at, for example, 100 hours at 1600°C. to afford an average grain size of about 8 microns. Further grain growth is limited by the thickness of the skeleton and the value of the density function approaches the lower limit of 0.5.

Typical commercial insulating fire bricks (Ipsen 3400 and Alundum L (trade mark))

have density functions of 0.08 and 0.05 respectively. A typical product from aluminium of this invention, even after heating 50 hours at 1700°C., has a density function of 0.74.

The following examples are given by way of illustration only:—

EXAMPLE 1

A melt of aluminium (AEC grade, 99.995% pure) heated to a temperature between 725 and 750°C. in an alumina pot under an atmosphere of argon is extruded through a one-hole alumina spinneret and the continuous filament, having an average diameter of about 0.005 inch, is collected in a loose batt. This filament is ductile, having an elongation at the break of between 5 and 35%.

Seventy-four grams of the filaments so prepared are hand-pressed into a mould $3 \times 6 \times 2$ inches, the bottom of which is perforated with $3/32$ inch holes. The resulting loose batt is

then thoroughly wetted with a saturated solution (25°C.) of fluxing agent identified in Table I. (In each case the percentage of fluxing agent is based on the total dry weight of the batt.) The wet batt is then compressed under

an 8000 pound load (about 410 psi), thereby removing excess solution. The compressed batt (3 × 6 × 0.41 inches) is removed from the mould, wiped dry and dried in a vacuum oven at 150°C. for 16 hours.

10

TABLE I

Fluxing Agent	% Agent (Based on total dried wt.)
(a) $\text{SiO}_2/\text{Na}_2\text{O}=3.25$ (ortho)	29.5
(b) Na_2CO_3	21.4
(c) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Borax)	22
(d) Na_2HPO_4	36

The dry batt is then placed in an electrically heated muffle furnace at 150°C. with an air atmosphere. The temperature is raised from room temperature to 600°C. over a period of about 4 hours, kept at 600°C. for 48 hours, raised to 1000°C. over a period of 2 hours and heated at 1000°C. for 1 hour.

The cooled structure of each run has some globules of metallic aluminium adhering to it which are removed by hand picking and melting (usual total of about 1 gram). The plate is about 6.02 × 3.13 × 0.45 inches, is dark grey, has the appearance of a solid ceramic, is opaque to light, hard and is permeable to air. The original fibre structure is visible on the surface. The plate of (a) has a hardness of approximately 12 on the modified moh scale, weighs 177 grams (1.31 gram/cm³ bulk density

or 81.6 pounds per cubic foot) and has a flexural strength of 1220 pounds per square inch (or 3720 per square inch when correction is made for density). The density of the solid phase is 3.4 gram/cm³ so that the plate contains 61.5% by volume of voids. Exposure of any of the plates to a natural gas/oxygen flame (approximately 2400°C.) for 1 minute causes no cracking or any other visible effects, demonstrating excellent resistance to thermal shock. A commercial sample ($\frac{3}{8}$ inch thick) of an electrically fused aluminium oxide cracks in two when exposed to such a flame. The bulk densities and flexural strengths (both "normal" and "density corrected" in pounds per square inch are reported in Table II for those samples upon which these properties are measured.

TABLE II

Bulk Density (g/cm ³)	Flexural Strength (psi)	
	Normal	Porosity Corrected
(b) 1.14	1200	4210
(c) 0.83	470	2260
(d) 1.22	1670	5480

Each of the plates is unaffected by boiling water, 50% aqueous NaOH, and concentrated H₂SO₄, while exposure to 50% aqueous HF at 100°C. for 2 hours extracts only 5% of the original weight, the residue being still strong and useful.

X-ray diffraction patterns of the product formed by (a) show a strong pattern for alpha alumina, the presence of some aluminium nitride and the absence of any aluminium. A crystalline silicon pattern is observed.

When the process is modified by a four-hour heating at 600°C. instead of a forty-eight hour heating at this temperature less complete oxidation occurs and the product has a (.7 to .9gm/cm³) lower bulk density. When the surface is ground (a diamond or garnet wheel required) it is noted that the fibres are hollow. A photomicrograph of the ground surface at a magnification of about four times is shown in Figure I.

By varying the amount of compression and

hence the density of the wet batt, plates are obtained having bulk densities of from about 0.2 to 3.5 gm/cm³.

- 5 Omission of the fluxing agent in the above process results only in a very thin layer of oxide on the metal with no bonding between particles.

Using fluxing agent (a) and following the

procedural technique employed as taught above (with a 600°C. heating period of 48 hours), various types of non-pellicular aluminium forms are employed to form products of the present invention. The shapes are identified in Table III and the measured properties in Table IV.

TABLE III

Aluminium Form	Particle Dimensions (mils)	Amt. Used (grams)
(e) Wool, soft, fine	*4 × 10	74
(f) Wool, coarse	*5 × 30	70
(g) Filaments (1/2% Si)	**5	48
(h) Filaments, commercial (Alloy No. 1100)	**6.4	50
(i) 1/2" staple, commercial (Alloy No. 6061)	1 × ca. 15	35
(j) +Carpet tacks, 1/2"	Not determined	Not determined

* Cross-sectional dimension

** Diameter

+ Cylindrical mould 2—1/2" diameter, 3/8" deep is stuffed full. Final structure weighs 20 grams. 32 grams of Al melts out.

Each structure has an excellent thermal shock resistance although (g) shows a decrease in strength after the thermal shock test.

TABLE IV

Bulk Density (g/cm ³)	Normal	Flexural Strength (psi) Density Corrected
(e) 1.30	1200	3700
(f) 1.47	1000	2725
(g) 0.98	1610	6310
(h) 1.19	1480	4980
(i) 1.13	1750	6200
(j) 0.55	Not measured	Not measured

- 20 Satisfactory products are also obtained when the sodium ortho silicate is diluted 1:1 with water (less than 15% of agent in composite).
 25 When using less concentrated solutions, the addition of a thickening agent is helpful to assure uniform coatings and retention of the fluxing agent on the metal.

EXAMPLE 2

(a) A laminate with alternating layers of aluminium foil and sodium silicate (applied as a concentrated aqueous slurry) is formed from 100 six-inch strips (71.4 grams) of 0.001 × 3 inch aluminium foil. It is placed in the 3 × 6 × 2 inch mould described in Example 1, subjected

to a pressure of 410 pounds per square inch and heated at 150°C. for 48 hours while still in the mould. After drying under vacuum for 16 hours, the structure is heated for 4 hours at 600°C. and 2 hours at 1000°C. as in Example 1. A strong sheet having a bulk density of 1.92 gm/cm³ and excellent thermal shock resistance results. Although the aluminium is not completely oxidised under these conditions, metallic aluminium does not melt out due to the nature of the structure.

(b) Another structure formed in the same mould in the manner taught above from 27 sheets (116 grams) of aluminium with cross sectional dimensions of 0.006 x 3 inches, has a bulk density of 2.71 gm/cm³.

(c) Commercial aluminium foil of 0.006 inch thickness is crimped by passing it between two intermeshing rolls each 3" in diameter and bearing 144 teeth on its surface. The crimped product in side view has the appearance of alternating equilateral triangles having an altitude of about 30 mils. The crimped foil is coated on both sides with the sodium silicate solution of (a) above and then about 25 alternate layers of the crimped foil and the uncrimped foil are placed together. There is sufficient adhesion due to the fluxing agent to hold the composite. The composite is dried in 150°C. vacuum oven and is then fired at 600°C. for about 48 hours and then for an additional 1 hour at 900°C. The oxidation is complete and no aluminium melts out of the product.

The final product, the edge of which is illustrated in Figure II, has a bulk density of 1.23 gm/cm³, has a flexural strength (density corrected) of 11000 psi transverse to the lamina. It has excellent thermal shock resistance and has the further advantage that prolonged exposure to a 2400°C. flame results only in the melting or corroding of a hole in the top layer of the laminate so that this structure provides an excellent flame-proof barrier.

EXAMPLE 3

A loose batt of the aluminium fibres of items (a) to (h) of Example 1 is hand-pressed around a large crucible to form a preform of the fibres in the shape of a crucible having a bulk density of about 0.38 gm/cm³. This is dipped into the sodium silicate solution of item (a) of Example 1, the excess wiped clear and the composite structure dried. It is then fired as in Example 1 to obtain a coherent strong structure having a bulk density of 0.72 gm/cm³ which is so porous that it transmits light.

EXAMPLE 4

Aluminium fibres of items (a) to (h) of Example 1 are moulded under 170 psi to give a wafer weighing 5.65 grams, 2 1/4" in diameter and 1/8" thick. The wafer is saturated with the sodium silicate solution of item (a) of

Example 1, diluted with 1 part and dried at 150°C. in a vacuum oven. The dried wafer is heated in 600°C. oven under an air atmosphere for 16 hours followed by a 30 minute treatment at 650°C. The wafer is removed from the oven, cooled, weighed (6.20 grams) and then reheated at 650°C. for 1 hour and then the temperature raised to 700°C. and an atmosphere consisting of oxygen/argon, 40%/60% by volume is passed through the oven for 1 hour followed by a 1-hour treatment at 800°C. under the same atmosphere and then a subsequent 20-minute treatment at 850°C. under the same atmosphere. The cooled wafer weighs 7.53 grams. A few small globules of aluminium (0.26 gram) are removed. The wafer is then refired at 950°C. for 1 hour. After this firing it weighs 9.33 grams. The wafer is then refired for 16 hours at 950°C. to give a final product weighing 9.41 grams. Based on the weight of aluminium remaining in the structure, the oxidation has proceeded to 73% of theoretical. The sodium silicate used, based on the weight of the metal remaining in the structure, is 9.9% of the aluminium or 0.014 mols of the fluxing agent per mol of the metal. The product is strong and has excellent thermal shock resistance to a 2400°C. flame. A photomicrograph of the surface of the structure, magnified about four times, is shown in Figure III. Globules of unremoved aluminium are visible along the edges of the photograph.

EXAMPLE 5

Approximately 2.5 grams of aluminium fibres (as employed in Example 1a, except in items f, g, k and m wherein commercial aluminium staple is used containing 1.2% manganese) is mixed with a water solution or slurry of the fluxing agent identified in Table V and the wet mass moulded into a 1 1/8" diameter wafer under about 410 pounds per square inch. The wet wafers are placed on a clay plate and dried in air in an electrically heated oven at temperatures noted below, for the period indicated.

Items b, d, j and n: 110
260°C. for 16 hours, then
625°C. for 16 hours, then
850°C. for 18 1/2 hours.

Items c, e, h, i and l: 115
600°C. for 2 hours, then
860°C. for 12 hours, then (for c and h only),
1000°C. for 16 hours.

Items f, g and m: 120
270°C. for 17 hours, then
600°C. for 24 hours, then
850°C. for 30 hours, then
1000°C. for 16 hours.

Items a and k:

600°C. for 16 hours, then
860°C. for 16 hours.

- 5 Table V reports the amount of fluxing agent (dry basis) on each item (determined by weighing after heating periods below 800°C.) and the percentage weight gain based on the theoretically possible gain after the high temperature (i.e. above 800°C.) cycles. It
10 will be noted that a second high temperature cycle was applied only to items, c, f, g, h and m. Control runs (i.e. no fluxing agents)

of the pure aluminium items disclose no weight gains on heating at 850°C. A control of the commercial staple (1.2% manganese) discloses a weight gain of 6% of that theoretically possible after 30 hours at 850°C. and 32.5% after 16 hours at 1000°C. Each control structure was crumbly with little strength.

Melting points are determined on the wafers after the final heat cycle by applying a natural gas-oxygen flame to the surface and estimating the temperature with an optical pyrometer. The samples do not crack or erode during the exposure to the flame showing the excellent thermal shock properties of these products.

TABLE V

Item	Fluxing Agent	*Wt. Flux (%)	+++Flux	++ Wt. gain (%) High. Temp.		Melt Point °C.	Crush Strength (psi)
				1st	2nd		
a	**LiOH	18.3	25.6	79		1875	1000
b	**Na ₂ O ₂	14	5.7	67		1650	560
c	KOH	13	7.1	-1	49	1560	1380
d	Ca(OH) ₂	30	15.8	62		1660	900
e	Sb ₂ O ₃	40	6.2	62		1475	520
f	+Bi(NO ₃) ₂	3	0.19	76	83	1925	450
g	Na ₂ B ₄ O ₇	14	2.2	26	95	1850	850
h	NaAlO ₂	54	31.4	70	72	1775	440
i	Na ₂ CO ₃	13	3.6	43		1750	1300
j	Na ₂ SiO ₂	29.8	9.4	60		1430	1400
k	PbSiO ₃	76	30			2020	11000
l	Na ₂ SnO ₃	11	1.97	76		1775	800
m	Na ₂ HPO ₄	88	1.8	38	77	1610	190
n	Na ₂ HAsO ₄	8.4	1.34			1770	

* Based on total weight

** Applied dry

+ Postulated to form BiO in reaction

++ Calculated as % wt. gain in converting the amount of Al in wafer to Al₂O₃

+++ $\frac{\text{gram moles flux}}{\text{gram atoms Al}} \times 100$

Items d, j and m exude globules of aluminium amounting to 5.6%, 77% and 1% of the original metal respectively. The other items do not lose aluminium.

5 EXAMPLE 6

A 25 gram mass of annealed fine nickel turnings (about 6 mil average diameter) are pressed into a wafer under 1900 psi pressure, saturated with sodium ortho silicate and dried.
10 The dry preform (30 grams, 0.046 moles of the agent per gram atom of nickel) is heated from 600°C. to 1000°C. and then at 1000°C. for 16 hours to yield a strong, coherent structure (36 grams) having a bulk density of 2.14 gm/cm³.

15 The use of a higher pressure on the preform (4500 psi) affords a similar product with a bulk density of 3.11 gm/cm³.

EXAMPLE 7

20 Shavings of titanium (about 3 x 3 mil cross section and 0.1 to 1 inch long) are annealed at 500°C. under a vacuum. The ductile metal (5.20 grams) is moulded into a wafer 2.25 inches in diameter by $\frac{1}{8}$ inch thick under 3000 psi. The porous wafer is vacuum impregnated with sodium ortho silicate (40° Be). The excess fluxing agent is wiped off and the wafer dried at 150°C. in a vacuum oven. The dried wafer (7.30 grams containing 28.8% of the dried flux) is heated in an oven with the temperature being gradually raised from 300 to 550°C. in 1 hour. Air at the rate of 1 cubic foot per hour is circulated through the oven. The wafer is then heated 16 hours at 800°C. It weighs 7.90 grams. Heating 3 hours at 1000°C. causes a further increase in weight of 2.1 grams to approximately the theoretical weight gain for complete oxidation.
35 No further weight gain occurs after 6 more hours heating at 1000°C.

40 The above white product is hard, strong, abrasive resistant, and is not cracked or altered by a sudden exposure to a natural gas/oxygen

flame (2400°C. estimated). It has a bulk density of 1.79 grams/cm³ and a density of the solid phase of 3.54 grams/cm³. The substitution of 4.6% Cr₂O₃ for the above fluxing agent affords a similar product after 5 hours at 950°C. 45

Useful products are made from magnesium shavings and slit copper foil in a similar manner. Also, steel wool and 30% V₂O₅ or 30% MnO₂ gives a strong product by this process. 50

EXAMPLE 8

55 While the invention has been particularly exemplified in terms of a funicular or pellicular shape, it is possible to form a product having fair thermal shock resistance from powdered metal. Thus following the procedure of Example 1a, 31 grams of 200 mesh aluminium powder is substituted for the filaments of that Example. The structure has a bulk density of 1.49, a flexural strength of 31 psi at 1550°C. which when corrected for porosity is 83 psi. On being tested for thermal shock resistance it is noted that a small crack is formed on the back of the heated face. When the size of the granular aluminium particle is increased to 60 mesh, a stronger, more thermally stable product is obtained. Due to their higher flexural strengths and thermal shock resistant properties, the funicular and pellicular shaped products are preferred. 60 65 70

EXAMPLE 9

75 Commercial aluminium wool of 98.1% purity (1.1% manganese is the primary impurity) is annealed by heating at 650°F. for 1 hour. The annealed wool is then chopped into fine staple having an average length of less than $\frac{1}{4}$ inch in a Waring Blendor. The chopped wool is thoroughly mixed dry with various amounts of powdered magnesium oxide, chromic oxide and sodium acetate (all of reagent grade) in a double bladed home-type mixer as shown below:— 80 85

Starting Material Weight Ratio

Item	Aluminium	MgO	Cr ₂ O ₃	Sodium Acetate
a	2	1	1	0
b	1	1	1/2	0.6% of total wt.
c	1	1	0	2% of total wt.
d	1	1	0	0
e	2	1	1/2	

90 The well-mixed dry material (2600 to 3500 grams, depending on density) is loaded into a mould 9" x 4 $\frac{1}{2}$ " x 3" deep and compressed under 1500 psi.

The compressed bricks are removed from

the mould and given the following heat treatment in an air atmosphere.

1. 25° to 150°C. in two hours.
2. 150° to 600°C. by increasing temperature 25°/hour

3. 12 hours at 600°C.
 4. 600° to 650°C. in 1 hour
 5. 7 hours at 650°C.
 6. 650° to 1350°C. at an increase of 50°/hour.
 7. 48 hours at 1350°C.
 8. cool furnace in 24 hours and unload.
 A portion of each mixture is moulded into $\frac{1}{4}'' \times \frac{1}{4}'' \times 2''$ test bars and submitted to the same firing schedule.
- The fired bricks and test bars are extremely hard, strong, resistant to abrasion and correspond closely to the dimensions of the unfired pieces. The maximum change observed is a 4% increase in the length of brick c.
- Properties measured on the test bars are given below:

	Bulk Density gram/cc.	Flexural Strength, psi.		Hot Load Subsidence
		25° C.	1550° C.	
a	1.80	1970	3560	2%
b	1.96	1530	1030	6%
c	1.65	738	479	1%
d	1.75			
e	1.99		2810	

- The hot load subsidence is measured according to ASTM C16 schedule 7, modified to use a cylindrical sample $2\frac{3}{4}''$ in diameter by 2" thick.

- Flexural strengths are measured on 1" spans at room temperature (about 25°C.) and in an oven at 1550°C.

- Examination of cut sections of the brick of item c above under a petrographic microscope shows that the brick is a cellular body having a continuum consisting essentially of a substantially homogenous refractory composed of alumina and magnesia spinel. The crystals of the continuum are extremely small with only a few as large as 5 microns in diameter. The cells of the brick are substantially isolated from one another. Most of the cells are filled with unreacted magnesia. The remainder of the cells are empty and correspond to the shape of the original metal fibres. Treatment of the sample with 80°C. formic acid for 60 hours extracts 22% of the weight and leaves a strong continuous skeleton of the spinel. Note: Item e is made with aluminium grained ingot of a particle size such that it passes through a 28 mesh sieve and is retained on a 42 mesh screen.

- The preparation of item c illustrates the use of a preferred fluxing agent. This product has a weight gain corresponding to 92% conversion of the aluminium. It has a uniformly dense cross section. Item d which used part of the magnesium oxide as a fluxing agent only shows a 63.5% conversion and has a very dense skin with a soft friable centre. Both products are strong and useful as refractories.
- The above procedure may be used to make compositions corresponding to:

Al ₂ O ₃	10 to 66%
MgO	11.5 to 90%
Cr ₂ O ₃	0 to 58.5%.

where the sum of these three components is equal to 98—100%, by weight. This class of refractories is especially useful for applications where a resistance to high temperature and corrosive environment is required. The basic open hearth steel furnace, especially those using oxygen lances, is an example of such applications.

The integral skeleton of items a and b is primarily composed of a solid solution of Cr₂O₃ in spinel. Items c, d and e have skeletons of spinel. The latter has some inclusions of a solid solution of Cr₂O₃ in alpha alumina.

EXAMPLE 10

This example shows the outstanding physical properties of the products of this invention.

Items a to f are made using aluminium metal according to the previous examples under the conditions defined in Table VI. Item d is made into a very low density structure fired at 800°C. to a 35% by weight conversion of aluminium. The partially converted structure is then broken into particles about 10 mils long, compacted and refired under conditions shown.

Items g, h and i are commercially available samples of refractories of similar compositions as identified in Table VII. Item g analyses 81% Al₂O₃, 17% SiO₂ and 1.6% Na₂O. Item h analyses 99% Al₂O₃ and 0.6% SiO₂. Item i analyses 97% Al₂O₃. Items g and h are presumed to be bonded hollow alumina spheres.

Item i is presumably made by firing a foamed mixture.

5 Table VIII compares characteristics and properties of the samples identified above. The superior flexural strength of the products of this invention over items g—j obviously presents a difference in kind. In addition to the

characteristics reported in the tables, it is noted that the average grain size of the aggregate particles of samples a—f inclusive, is about 1 micron or less. This compares with a 50 micron and 6.5 micron grain size in the structure of samples h and i respectively. 10

TABLE VI

Sample	Metal Form	Flux agent	Amt. Flux ⁺	Firing Cond.	
				Max. Tem.(°C.)	Period (hr.)
a	Flake	Sod. acetate	1.5	950	16
b	Fibre	Sod. acetate	1.5	1000	3
c	Wool*	Pot. oxide	0.5	1600	1
d	Wool*	Sod. oxide	0.5	1250	4
e	Fibre	Sod. silicate	18.0	1500	4
f	Fibre	Sod. silicate	20.0	1000	8

* Commercial grade

+ % by wt. based on metal used

TABLE VII

Sample	Trade Name
g	Alfrac B1
h	Alundum L
i	Ipsen 3400

TABLE VIII

Sample	Bulk Density gm/cm ³	Porosity %	Average Cell Size (Microns)	Flex. 25° C.	Strength 1550°C.	Abrasion Loss (gms.)
a	1.10	48.0	167	720	1330	—
b	1.90	46.5	85	2420	1704	—
c	1.42	61.3	87	1710	2200	0.02
d	2.05	45.0	129	11000	2750	0.01
e	1.62	55.8	119	—	1020	—
f*	0.74	79.6	—	1140	—	—
g	1.22	68.7	100—150	230	25	0.4
h	1.19	70.0	80—150	250	16	0.6
i	0.46	88.3	130—630	40	nil	1.7

* Photomicrograph of fragmented elevation shown in Figure V.

EXAMPLE 11

This example shows the effectiveness of the flux employed in the process using aluminium as the metal in the green structure. In each of samples a—o inclusive of Table IX, about 1.5—4.5 grams of a commercial aluminium staple (average diameter of about 0.010 inches and about 0.5 inches long) containing 1.2% manganese is formed into a $\frac{1}{4} \times \frac{1}{4} \times 3$ inch bar. A measured amount of an aqueous solution of a metallic acetate flux (a precursor of the oxide) as identified in the Table IX is dropped onto the aluminium bar which is then dried at 150°C. Each dried bar has an apparent density of about 0.5 and 1.5 gms/cm³ (80 to 45% porosity). The dried weight of each bar is used to calculate the per cent of metal oxide based on the weight of aluminium that is present under the firing conditions. The acetate salts are known to convert quantitatively to the oxides on heating in air at about 500°C.

The dried bars are placed in electrically

heated furnaces with an air atmosphere and heated at various temperatures for the periods (hours) indicated in Table IX. The weight gain reported is in terms of the percentage of that theoretically possible.

The products of items a—j inclusive are all hard, strong, abrasive resistant articles having a continuous skeleton of alumina. They have apparent densities of 0.78 to 2.3 gms/cm³ (porosities of 42 to 80%). The original fibres are bonded together by alumina and cannot be picked out of the structure. Similar structures are also made at 750°C. with lithium and sodium acetate as fluxes (0.5 and 1% respectively). All items made without a flux (k—o inclusive) are soft, friable and can be easily picked apart with a needle or tweezers to yield the original fibres with only a thin coating of alumina.

Other fluxes such as NaOH, NaAlO₂, sodium potassium tartrate, sodium methoxide and barium stearate or their precursors are also suitable.

25

30

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40

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TABLE IX

Sample	Flux	% Flux	Temperature (°C.)	Period	Weight gain
a	Li ₂ O	1.5	900	5—6	83
b	"	0.4	950	3	60
c	"	0.06	1000	15—16	17
d	Na ₂ O	0.5	800	24	86
e	"	0.35	900	16	50
f	"	0.5	1250	"	78
g	K ₂ O	0.45	880	24	92
h	MgO	1.5	1300	40	64
i	BaO	1.0	1000	1	30
j	"	1.2	1300	40	57
k	None	—	850	15—16	1
l	"	—	"	40	6
m	"	—	1000	24	5
n	"	—	1150	15—16	8
o	"	—	1250	"	24
p	"	—	"	+40	28
q	"	—	1300	15—16	12
r	"	—	"	40	19
s	"	—	"	66	31

EXAMPLE 12

Commercial aluminium wool (alloy 3003) is picked for 15 minutes at 50—60°C. in a solution consisting of 0.2 gram chromium sulphate, 14.4 grams potassium dichromate, 7.75 grams sodium hydroxide and 155 grams of water. The aluminium wool is removed and washed well with water to remove all traces of yellow colour and dried. The emission spectrograph on the treated wool shows less than 200 parts/million potassium, 50—250 parts/million sodium, and 1—5% chromium. 44.5 grams of the pickled aluminium wool is chopped to staple in a 1 gallon Waring Blender and compressed in a mould at 2,000 psi to a block 2½ inch in diameter by 2 inches high.

The block is placed in an electrical furnace at 725°C. for 16 hours, weight 43.4 grams. It is refired at 850—950°C. for 24 hours,

weight 48.7 grams. The block is then placed in a Sclas gas furnace and heated at 1200°C. for 1 hour and 2 hours at 1600°C. The final weight is 71.2 grams or 67.5% of theoretical gain. 25

Test bars cut from the fired block show a porosity of 49% and have a flexural strength of 360 psi at 1550°C. (corrected to 710 psi based on porosity). Microscopic examination of the broken bars shows a well integrated homogenous alumina skeleton containing a solid solution of Cr₂O₃. 30

EXAMPLE 13

Zirconium metal turnings (10.1 grams) are compressed to a 2½ inch diameter wafer with 40° Bé sodium silicate solution at 170 psi. It is air dried followed by drying at reduced pressure at 150°C. and redipped in sodium silicate and dried again. The dry wafer is 40

placed in a furnace at 200°C., after 1 hour has swollen in size due to foaming of the silicate. It is repressed at 1400 psi (19.5 grams). It is heated for $\frac{1}{2}$ hour to 800°C. in air with no visible change. It is changed to an atmosphere of 6% O₂ in argon and heated to 1100°C. where it is visibly attacked. After 1 hour the oxygen content is increased to 15% (in argon). After an additional $\frac{3}{4}$ hour the oxygen content is increased to 20% (in argon) still at 1100°C. The total gas flow is about 1 cfh. After an additional $\frac{1}{2}$ hour of heating the oxygen is increased to 40% in argon for 15 minutes.

The product is a hard, strong batt (22.4 grams or 83% of theoretical conversion) with an apparent density of 0.84gm/cc.

EXAMPLE 14

This example illustrates preparation of the structures lacking in a continuous skeleton of *in situ* formed oxide. In this example aluminium metal in the form of powder and pieces of foil is used as identified in Table XI. The powder is Alcoa (trade mark) No. 123 atomised Al which has a particle size such that 85% is less than 325 mesh and 100% is less than 200 mesh. The foil is Alcoa No. 11458 cut to a shape 5 mils \times 10 mils \times 190 mils. The filler refractories of Table XI are more particularly identified in Table X.

Items a and b are prepared by mixing the filler refractory with a 50% aqueous solution of the flux agent and drying. This dried, powdered mixture is then mixed with the aluminium foil and 15 parts of hexane per 100 parts of mixture. Items c—h inclusive are prepared by thoroughly mixing the filler refractory and the aluminium powder, adding the flux agent (containing 4 parts of ethanol), thoroughly mixing and then adding (as a temporary green bonding agent) 4 parts of

commercial rubber cement diluted with 4 parts of benzene. The green objects after drying (i.e. heating at 600°C.) have porosities of between about 28 and about 50%.

The homogenous wet mixture is placed in a steel mould of 2.25 inches diameter and compressed under about 5000 pounds per square inch (psi pressure). The moulded disc (about 0.25 inches thick) is removed from the mould and placed in an electrically heated furnace and heated as follows: 25—600°C. for 12 hours, 600°C. for 8 hours, 600—1000°C. for 4 hours, 1000°C. for 4 hours, 1000—1400°C. for 6.5 hours and 6 hours at 1400°C. followed by a 12 hour cooling period.

The fired discs are measured, weighed and cut into $2 \times \frac{1}{4} \times \frac{1}{4}$ inch samples for flexural strength determinations. The observed results are reported in Table XI.

After firing, items a, b and c conform closely to their original shapes with no warping and expand linearly (diameter) in the amounts of 10, 8 and 0%, respectively. Items c and f show appreciably greater weight gains at the lower temperatures (1000°C.) than do their control, item e. This permits the use of much lower firing temperatures with the flux containing process to avoid fusion of the filler refractory at this stage. For example, item c had a weight gain (uncorrected for loss of binder and liquids) or 63% of theoretical for the oxidation of the aluminium after the 1000°C. firing. Item e (containing no flux) showed no weight gain under the same conditions. Another observation is that after the 1000°C. firing items c and f have very smooth surfaces whereas the control (item e) is quite rough and has numerous globules of unreacted aluminium on the surface.

Similar strong structures are obtained by replacing the flux used with lithium hydroxide, potassium oxalate or cesium nitrate.

TABLE X

Refractor Identity	Sieve Sizes (mesh)	Magnesite : Magnesia	
		*Dead Burnt Magnesite	+Fused Magnesia
A	40 — 60	150	1:1
B	150 — 200	40 — 60	1:4
C	None	40 — 60	0:1

* No. 1 calcined, 98% MgO.

+ No. 12706, 99.3% MgO and 0.4 SiO₂

TABLE XI

Sample	Aluminium *Shape	Parts	Refractory +Type	Parts	**Flux Agent Parts	Flex Strength at 25°C. psi	Porosity %
a	F	9	A	91	3	550	36
b	F	16	A	84	3	1400	43
c	P	5	B	25	0.6	1650	28
d	P	5	C	25	1.2	2750	41
e	P	5	C	25	0	370	34
f	P	5	C	25	0.6	1030	28
g	none		C	25	0.6	50	44

* Foil or Powder

+ cf. Table X

** 50% aqueous NaOH except (d) where 50% aq. sod. acetate is used.

EXAMPLE 15

The procedure of samples c—g of Example 15 is applied to a mixture of 15 parts of the aluminium powder of Example 15, 85 parts of silicon carbide of 30 to 120 mesh and 2.5 parts of sodium acetate. Samples cut from the resulting disc have a flexural strength of 5950 psi at 25°C. A control disc made in the same manner but with no aluminium has a flexural strength of only 230 psi.

By substituting granular tantalum carbide, or stabilised zirconium oxide for the silicon carbide in the above catalysed process, similar strong aggregates lacking in a continuous skeleton of *in situ* formed oxide are made.

Theory

While applicant does not wish to be bound by any particular theory, it is believed that, under the conditions of the oxidation the fluxing agents applied to the surface of the metal particles act to release the protective oxide coating which is characteristic of the metals within the recited group, as rapidly as these coatings form, thereby permitting progressive oxidation through the cross-sectional area of the metal particle to any desired extent. In addition to promoting the release of the protective oxide coatings from the metal surfaces, the fluxing agent also appears to act as an oxidation transfer agent, thereby hastening the oxidation process. Oxygen-containing salts within the broad class of metal salts defined are particularly valuable as fluxing agents. When size and density of metal particles in the green form permits, the simultaneous production and release of the protective oxide

coating from each particle source tends to diffuse one into another, thereby providing a mutual molecular intradistribution of oxide that results in a self-bonded final structure. During the process, the oxidised form of the nominal element of the fluxing agent is at times diffused through the metal oxide which is formed *in situ*. At other times the fluxing agent is lost to the atmosphere during the firing. In certain combinations of metal and refractory fillers, chemical reaction occurs between the materials fired to produce spinels for example.

Process Conditions

As previously pointed out, prior to heating the shaped metal aggregate particles in an oxidising atmosphere, the surfaces of the aggregate particles are intimately contacted with a fluxing agent as previously identified. The agent may be applied to the surface of the metal particles prior to their aggregation or at any other time prior to the final heating operation. Preferably the agent is applied to a "loose" aggregate, i.e. an aggregate less compact than the shaped one to which the firing operation is applied. Such a technique assists in efficient application of the agent to the metal surface with good distribution through the body of the aggregate. When using funicular or elongated shapes the aggregate is compacted into a loose batt or preform having a bulk density of 0.01 to 75% of the solid metal. The particles in the batt are then contacted with the fluxing agent. The agent may be applied dry, in solution, as a gas or as a melt. The manipulative technique of contact-

ing the metal surface with it is not critical. Thus it may be powdered or sprayed upon the metal, or the metal may be dipped in a solution of the agent or its melt or powder. It is conveniently done using a concentrated aqueous solution or slurry. The use of pressure and/or vacuum to assist in uniform and complete distribution of the agent over the particle surfaces is often advantageous. Furthermore, when using dilute solutions, the addition of a thickener such as sodium carboxy methyl cellulose may be advantageous. Particularly where the proportion of metal to filler refractory is low, the fluxing agent may be applied to the filler refractory and the metal shapes added to the moist mixture as is exemplified in Examples 15a and b. In cases where the flux itself does not act as a binder and especially when using 20 to 50% of aluminium in the form of slit foil or granules, it is advantageous to add minor amounts of water, ethyl alcohol, ethylene glycol, acetone, aqueous solutions of carboxy methyl cellulose, rubber, gum arabic, polyvinyl alcohol, polyvinyl pyrrolidone, natural gums, or glue to increase the green strength of the shaped object. A self-bonding additive such as Sorel cement ($2\text{MgO} \cdot 1\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) or a mixture of magnesium oxide and saturated sodium chloride can also be used for this purpose. Preferably a material is used that will burn out under the firing conditions. From 0.1% to 2% binder is usually adequate. The amount of agent to be employed will vary depending upon the nature of the metal as well as the nature of the agent. The fluxing agent is calculated on the basis of the metal oxide that it forms in those cases where a metal oxide precursor is used. The metal oxide or hydroxide can vary in amount from 0.05 to 20% based on the total weight of the green structure. Preferably from about 0.2 to 5% is used in forming the skeleton-like shaped structures whereas from about 0.1 to 2% is preferred in forming the non-skeleton structures. Higher concentrations of fluxing agent may be employed but are generally avoided unless the fluxing agent may also act as a filler refractory to prevent undue lowering of the melting point of the final structure and loss of strength at elevated temperatures.

After application of the fluxing agent to the loose batt of metal, the aggregate is then compression moulded to the final desired shape. When forming structures containing about 20% by weight metal and more in the green form, the use of a ductile metal is preferred for improved formability at this stage, especially when intricate final shapes are desired. The moulded object is then dried. When making a predominantly skeleton type structure the moulded, dried green object conveniently has a porosity of from 25 to 85% at the firing temperature of 700 to 1600°C. in order to permit oxygen to penetrate through-

out the shaped object. This is especially important when massive objects as fire bricks are being made. When making the predominantly non-skeleton or web-like structures the dried green object should have a porosity of between about 20 and about 70% at the firing temperature of 600 to 1050°C. in order to permit penetration of oxygen.

The dried "green" moulded object is then heated in an oxidising atmosphere such as air, oxygen or mixtures of oxygen and inert gases at a temperature of at least 400°C. but below the ignition temperature of the metal at the concentration of oxygen employed. The exact conditions for firing will depend upon the green porosity of the shaped object, the amount of metal, the amount and kind of fluxing agent and the temperature. These interactions and variations among them will be apparent to one skilled in the art. In order to obtain substantially complete and homogenous oxidation of the metal particles, the above-mentioned variables should be selected so that a spontaneous and rapid ignition does not take place, or a spontaneous and rapid reduction of the non-aluminium constituents does not occur. In general at least the first stages of oxidation should be carried out at a relatively low temperature. For example, a temperature of about 700° to 1050°C. for a period of about $\frac{1}{2}$ to 48 hours can be used with aluminium in combination with as little as 0.1 to 3% of an alkali metal oxide or hydroxide. The less active fluxing agent such as MgO in the amount of 0.1 to 10% will require from 1 to 72 hours at temperatures of 1000° to 1350°C. or higher. For metals having a relatively low melting point, such as aluminium and magnesium initially, until a stress bearing oxide film develops which holds the moulded shape of the aggregate during subsequent further oxidation at a higher temperature.

The temperature and period of the heating step are co-related functions. They will vary widely depending primarily upon the nature of the metal, the nature of the fluxing agent, the concentration of the fluxing agent and the nature of the oxidising atmosphere. In general, any temperature below the melting point of the metal may be employed, the higher temperatures favouring a decrease in the necessary period of heating. The heating is continued for a period of time sufficient to permit oxide growth which will result in a weight gain of at least 10% based on the metal in the green structure. The strength of the bond in the continuous skeleton type structure is believed due to the intra-distribution of oxide growth at a molecular level, i.e. to form a solid solution. The period of heating can be varied widely even with reference to any particular agent/metal combination, depending upon the type of final product desired. In general, the oxidation will be carried out at a temperature of from 600° to about 1000°C.

when using an atmosphere of air or an atmosphere containing an equivalent amount of oxygen and a normal amount of fluxing agent. As pointed out above, when using a metal with a low melting point, such as aluminium or magnesium, it is desirable to have a preliminary oxidation step at a temperature close to the melting point of the metal, as, for example, 16 hours at 600°C. or 2 hours at 700°C. In the latter case, the structure must be well supported so that a minimum of strain is put on the object and the molten aluminium is not extruded. The extent of this preliminary oxidation will also depend upon the dimensions of the metal particles in the structure. The previous remarks apply to a 5 mil diameter filament. After an initial shell of oxide has been formed, then the secondary or final oxidation can be carried out at a higher temperature which for aluminium or magnesium may be 850°C. for 4 hours or as high as 48 hours at 1000°C. When only a thin skin of oxide is formed initially, followed by heating above the melting point of the metal, unoxidised metal is exuded. Using this process on aluminium, the alpha crystalline form (corundum) is always formed regardless of the temperature used. Unoxidised metal may be melted out of the formed mass when particle morphology permits. This is an unusual phenomena which apparently results from the incompatibility of these metals and their oxides. When melted out, the metal appears in globules on the surface of the formed oxide structure from which it may be removed by abrasion, heat treatment, or the like. As much as 85% of the original metal employed may be recovered by this method. If a relatively thick skin of oxide is formed at the relatively low initial temperature, no metal is exuded on raising the temperature above the melting point, but a greatly increased rate of oxidation is observed. The two heating stages, when desirable, can be applied as separate steps, with or without cooling between stages. Alternatively, the temperature may be progressively raised through the range desired at a rate adequate to form the initial shell and thereafter provide either melting out of unoxidised metal or further oxidation at increased rate as desired. In addition to the removal of residual metal by heating above the melting point of the metal after partial oxide formation, an elevated temperature may also be used to change the crystalline form of the oxide. Subject to the aforesaid objects, the rate at which the temperature of the structure is raised to the oxidising temperature and/or above is not critical and will be controlled solely by the capacity of the heating furnace. Metals having relatively high melting point, such as nickel, iron, zirconium, copper, and titanium, can be placed directly in an oven at 800 to 1000°C. for a one-step oxidation. Regardless of the identity of metal however, it is essential that a rapid ignition

does not take place during the oxidation; for example, the use of 1100°C. in an air atmosphere causes a rapid ignition of a zirconium structure which gives a loosely matted batt of very low strength. However, when the same structure, using sodium silicate as a fluxing agent, is oxidised in an atmosphere containing only 6% oxygen at 1100°C., a strong coherent structure is obtained. It is also essential that the temperature employed during oxidation be below the melting point of the oxide of the metal forming the aggregate.

During the heating operation the shaped aggregate may be under compression or free from compressive forces. Generally it is preferred to permit the natural growth of the oxide, although some pressure will tend to improve the diffusion between contiguous particles. The particles forming the aggregate of the original structure may be in random or patterned arrangement. Thus, although the Examples using fibre are limited to randomly disposed particles, an orderly laydown of staple or tow may be employed to build up a suitable batt for conversion to refractory structures of the present invention. These fibres may be crimped if desired and conventional needling operations may at times be useful in forming dense or felted structures prior to oxidation.

Identity of Metals

Metals suitable for use in this invention are any yielding oxides that are refractory, i.e. having melting points above 1000°C. and possessing structural rigidity. Among suitable materials may be mentioned aluminium, beryllium, calcium, chromium, niobium, copper, hafnium, iron, magnesium, nickel, silicon, tantalum, thorium, titanium and zirconium. Aluminium is preferred for forming the continuous skeleton product previously described. Mixtures of particles of two or more different metals may be used as well as particles of alloys of the recited metals and alloys with other metals in which the recited metals constitute the major component. The metal used is preferably clean and free from grease and oil. In making the continuous skeleton product, the metallic shapes preferably have one dimension of from 0.5 to 125 mils, a second dimension of at least 10 mils, and a third dimension of at least 0.5 mil, both the second and third dimensions being at least equal to the first dimension. For example, if spheres of aluminium are used, they must have a diameter between 10 and 125 mils (between about 7 and 60 mesh). Cylindrical rods as fibres must have a diameter of between 0.5 and 125 mils and a length of at least 10 mils. The length is not critical and can vary from short staple to continuous filaments. In making the structures having little or no continuous skeleton, other shapes are satisfactory. In this regard it has been found that

the ratio of the surface area/volume expressed in mm^{-1} (i.e., reciprocal millimetre) can be used to designate particularly useful shapes. For convenience, this ratio is given below

for various spheres of aluminium. The ratio for a $190 \times 5 \times 10$ mil foil (as used in Example 15) is 24 mm^{-1} .

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Maximum Size Passing Mesh	Diameter of Sphere in mm	Surface Area Volume mm^{-1}
7	2.83	2.1
20	0.84	7
25	.71	<u>8.5</u>
60	.250	<u>24</u>
100	.149	41
200	.074	81
325	0.044	140

- 10 Shapes having ratios of 7 to 100 may be advantageously used with ratios of 10 to 80 being preferred. The use of shapes with ratios of 5 or less sometimes causes uneven bonding of the refractory. Particles of mesh size between 20 and 150 are preferred.

15 Identity of Fluxing Agents

- Suitable fluxing agents for use in forming the structures of the present invention are, as defined above, any of (I) an oxide of a metal other than the metal used for forming the said refractory oxide and (II) a precursor of the oxides of (I), the said oxides of (I) being of a metal from the class consisting of the alkali metals, the alkaline earth metals, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony and bismuth. The oxides and hydroxides of the alkali metals, and magnesium, strontium and barium are preferred, particularly for structures wherein aluminium is the metallic component. The oxides and hydroxides of the alkali metals are preferred for forming refractions of the non-continuous skeleton variety. Among suitable precursors of these materials may be mentioned the acetates, benzoates, bismuth thioglycolates, bisulphates, bisulphites, bromates, nitrates, nitrites, citrates, dithionates, ethylates, formaldehyde sulphonylates, formates, hydrosulphites, hypochlorites, metabisulphites, methylates, oleates, oxalates, perchlorates, periodates, persulphates, salicylates, selenates, silicates, stearates, sulphates, sulphites, tartrates, and thiosulphates of the recited metals. While not "per se" within the class of useful fluxing agents, these compounds do, under conditions of the reaction, yield compounds within the above defined class. Thus sodium

acetate, -benzoate, -bismuth thioglycollate, etc., will yield sodium oxide which is an oxide of an alkali metal. In addition, trialkyl tin oxide and lead silicate (PbSiO_3) are also useful as fluxing agents. Other fluxing agents can be found by means of the test cited below.

Test for Fluxing Agent

About 25 grams of the aluminium to be used in the process is placed in a 40 ml. alumina crucible ("Alundum"). The crucible is placed in an electric furnace to melt the aluminium, removed and the surface of the metal skimmed to remove any extraneous aluminium oxide. A pocket forms in the centre of the aluminium surface upon cooling. The major portion of a one gram sample of a powdered fluxing agent candidate (a metal oxide or hydroxide or a compound which may be expected to form a metal oxide under the conditions of the test) is placed in the pocket. A minor amount of the powder is placed so it contacts both the aluminium and the crucible at the edge. A control using powdered alumina is also prepared.

The crucibles are placed in an electrically heated furnace with an air atmosphere and heated at 1000°C . for 10 hours. The crucibles are slowly cooled and examined for a reaction. If the candidate is an effective flux at the first temperature tried, the test may be repeated at some lower temperature (e.g. 850°C .) to better classify the effective temperature. If no reaction occurs on the first trial, higher temperatures (e.g. 1300 and 1400°C . in turn) may be tried.

The most effective flux agents (class 1) are characterised by their complete disappearance, a darkening of the aluminium surface and the appearance of a black colour on the outside of

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the crucible. With less effective flux agents (class 2) the blackening of the crucible is not observed but (1) the surface of the aluminium is darkened and (2) the flux candidate does disappear and/or the aluminium has foamed in comparison with the control. Those candidates which do not fulfil the above requirements but which do at least partially fuse into the surface of the metal are considered class 3 fluxes.

If all of the candidate is still loose on the surface of the aluminium it is not considered to be a fluxing agent for this process.

The candidates must be restricted to substantially non-volatile compounds or else run under pressure in order to obtain valid results.

Following are some fluxing agents classified by this test:

TABLE XII

Candidate	at 850°C.	at 1000°C.	at 1300°C.
LiOH	Class 2	Class 1	
NaC ₂ H ₃ O ₂		Class 1	
K ₂ C ₂ O ₃ ·H ₂ O		Class 2	
Mg(OH) ₂			Class 2
Sr(OH) ₂ ·8H ₂ O			Class 2
BaCO ₃		Class 1	
V ₂ O ₅	Class 2	Class 2	
MoO ₃		Class 2	
WO ₃			Class 2
Na ₂ SiO ₃	Class 1		
NaOH	Class 1		

As pointed out above, the element of the fluxing agent within the defined classes must be other than the element of the particles of metal employed. This is demonstrated in the following example.

EXAMPLE 16

10 grams of 80—200 mesh aluminium oxide is mixed with 1 gram aluminium powder (maximum size .002 mm.). Enough water is added to obtain a slurry and $\frac{1}{4}$ gram of low viscosity carboxy methyl cellulose is added as a thickener. The mixture is dried overnight at 150°C. in the form of a wafer about 2½ inches in diameter and $\frac{1}{4}$ inch thick. The dry wafer is thereafter dropped into a hot furnace (1100°C.) in a 100% oxygen atmosphere. The wafer ignites and glows evenly. Oxidation is complete in just a few minutes. A very weak structure results. The temperature does not reach a high enough intensity to sinter or fuse the aluminium oxide.

Oxidising Atmosphere

The atmosphere of the firing operation must be oxidising in character. Most conveniently air is employed for this purpose. However, the process may be speeded up by enriching the atmosphere with oxygen or ozone. Other oxidising atmospheres which may be employed are argon-oxygen and helium-oxygen mixtures. The metal can also be converted to a nitride, boride, silicide or carbide to give useful products. When using aluminium as the metallic component of the green structure it is preferred to avoid the use of nitrogen containing gases.

Filler Refractories

As is illustrated above, the structures of the present invention may contain up to about 95% of a particulate, crystalline filler refractory. Generally these may be any of the carbides of aluminium, boron, hafnium, niobium, silicon, tantalum, thorium, titanium, tungsten,

vanadium, and zirconium; the nitrides of aluminium, boron, hafnium, niobium, tantalum, thorium, titanium, uranium, vanadium, and zirconium; the borides of chromium, hafnium, molybdenum, niobium, tantalum, titanium, tungsten, vanadium, and zirconium; or the oxides of aluminium, beryllium, cerium, hafnium, lanthanum, magnesium, uranium, yttrium, and the stabilised oxide of zirconium or composites of the above. Furthermore, when in sufficient concentration and of adequate size, many of the oxides used as fluxing agents can serve also as filler refractories. It is preferred that the filler refractory be of such size that the particles will pass an 8 mesh sieve and mainly be retained on a 200 mesh sieve. The use of smaller particles makes it difficult to convert the metal, particularly aluminium, completely, tends to yield products having undesirably high apparent densities, and is apt to produce an undesirably great shrinkage during the firing. The above filter refractories can be replaced in the unfired structures by their precursors which will yield the desired refractory during firing.

After Treatments

When a non-porous coating upon the refractory is desired, coatings such as aluminium oxide, zirconium oxide, titanium dioxide, tantalum or a silicide, may be applied by conventional metal spraying techniques. The voids of the refractory can also be filled with metals, other refractories, glasses or polymers, either by after treatment or by incorporating a material (such as fibrous potassium titanate) in the green form before firing. While glasses may be present, added in after treatment, or formed *in situ*, the structures of the present invention are characterised by crystallinity. Preferably about 90% by weight of the structure is crystalline.

Utility

The products of this invention are useful as structural components of apparatus which must withstand high temperatures, as bricks for furnace linings, insulating panels, crucibles, shaped abrasives, bearing materials, missile nose cones, catalysts and catalyst supports, tube sections, motor casings, bearings, electronic coil cores, electronic tube sockets, light weight rigid fire-resistant walls, rocket engine linings, jet engine exhaust linings and others.

The process of this invention may also be used to provide coatings of a refractory upon suitable surfaces. The mass of metal particles and flux may be fired in contact with the surface of the object to be coated.

The unfired or partially fired objects of this invention may be welded to each other by placing in intimate contact and firing further.

WHAT WE CLAIM IS:—

1. A crystalline refractory characterised by a porosity of from 20% to 90% and compris-

ing a rigid aggregate of metal oxide shapes having at least one dimension of from 0.5 to 125 mils, the oxide shapes being either (A) the oxide formed by the *in situ* oxidation with gaseous oxygen of aluminium, beryllium, calcium chromium, niobium copper, hafnium, iron, magnesium, nickel, silicon, tantalum, thorium, titanium, or zirconium or an alloy in which one of said metals constitutes the predominant component or (B) a composite of (A) and the oxide of a different metal than that recited in (A) which metal is an alkali metal, an alkaline earth metal, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony or bismuth, the composite containing from 4.6% to 99.95% by weight of metal oxide formed *in situ* and from 0.02% to 20% of the oxide of the said different metal, the crystalline refractory being further characterised by a residual metal content from the formation of (A) of no greater than 85%, and, when present, no more than 95% of a filler refractory as hereinbefore defined, the said filler being particulate, crystalline and substantially unfused.

2. A crystalline refractory according to claim 1, in which the oxide particles of the aggregate have a first dimension of from 0.5 to 125 mils, a second dimension of at least 10 mils, and a third dimension of at least 0.5 mil, both the second and third dimensions being at least equal to the first dimension.

3. A laminate which comprises a plurality of sheets of a crystalline refractory according to claim 1.

4. A laminate according to claim 3, in which alternate layers are crimped to produce a corrugated structure.

5. A crystalline refractory according to Claim 1 which has a substantially continuous integral skeleton of the *in situ* formed oxide.

6. A crystalline refractory according to Claim 1 containing at least 80% of particulate crystalline filler refractory.

7. A crystalline refractory substantially as herein described with reference to any of the Examples.

8. A process for forming a crystalline refractory which comprises intimately contacting the surfaces of (A) from 4% to 99.98% by weight of particles of aluminium, beryllium, calcium, chromium, niobium, copper, hafnium, iron, magnesium, nickel, silicon, tantalum, thorium, titanium or zirconium, or an alloy in which one of said metals constitutes the predominant component with (B) from 0.02% to 20% by weight of a fluxing agent which is either (I) an oxide of a metal other than those recited in (A) or (II) a precursor of the oxides of (I), the oxides of (I) being of an alkali metal, an alkaline earth metal, vanadium, chromium, molybdenum, tungsten, copper, silver, zinc, antimony or bismuth or (III) trialkyl tin oxide or lead silicate and (C) from 0% to 95% of a particulate, crystalline

5 filler refractory, the contacted mass of (A),
(B) and (C) having a porosity after removal
of volatile materials of at least 20%, and there-
after oxidising the metal in the contacted mass
with gaseous oxygen at a temperature of at
least 400°C. and, if the filler refractory is
10 present, below that at which the filler refrac-
tory fuses for a period of time sufficient to
give rise to a weight gain of at least 10%
based on the weight of the metal employed.

9. A process according to claim 8, in which
the metal or alloy (A) has a surface area to
volume ratio between 100 mm^{-1} and 7 mm^{-1} .

10. A process according to Claim 8 or 9,
15 in which oxidation is carried out at a tempera-
ture below the melting point of the metal.

11. A process according to Claim 8 or
9 in which oxidation is initially effected at a
temperature below the melting point of the
20 metal and when a relatively thick skin of
oxide coating has been formed upon the metal
particles, the temperature of oxidation is raised

to above the melting point of the metal until
substantially all the metal is converted to
the oxide.

12. A process according to Claim 8 or 9
in which oxidation is initially effected at a
temperature below the melting point of the
metal and when a relatively thin skin of oxide
coating has been formed upon the metal
30 particles, the temperature of oxidation is
raised to above the melting point of the metal
to melt out the metal from within the oxide
skin, thereby producing a hollow structure.

13. A process for forming a crystalline
35 refractory substantially as herein described
with reference to any of the Examples.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press
(Leamington) Ltd.—1965. Published by The Patent Office, 25 Southampton Buildings,
London, W.C.2, from which copies may be obtained.

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FIG. I

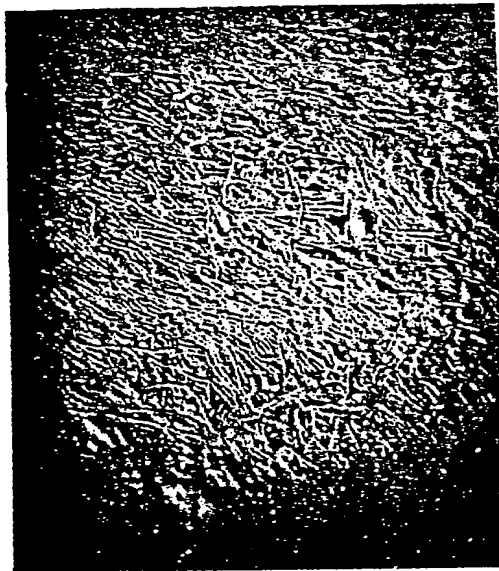
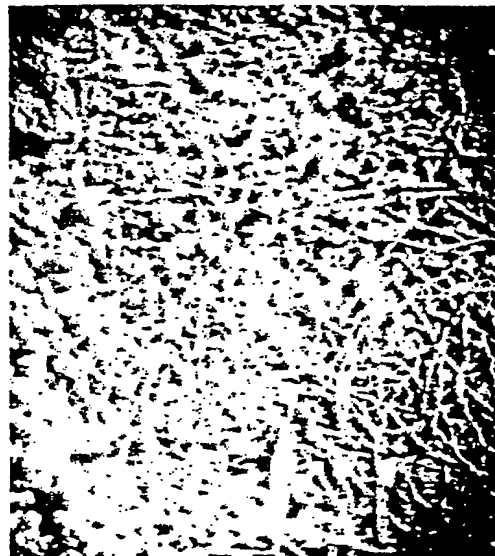


FIG. II



FIG. III



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4 SHEETS

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SHEETS 1 & 2

FIG. IV



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SHEETS 1 & 2

FIG. I

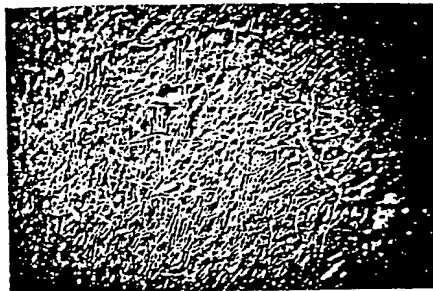


FIG. II



FIG. III

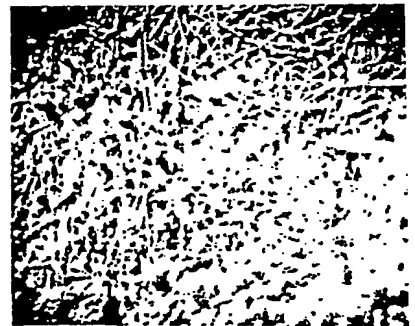
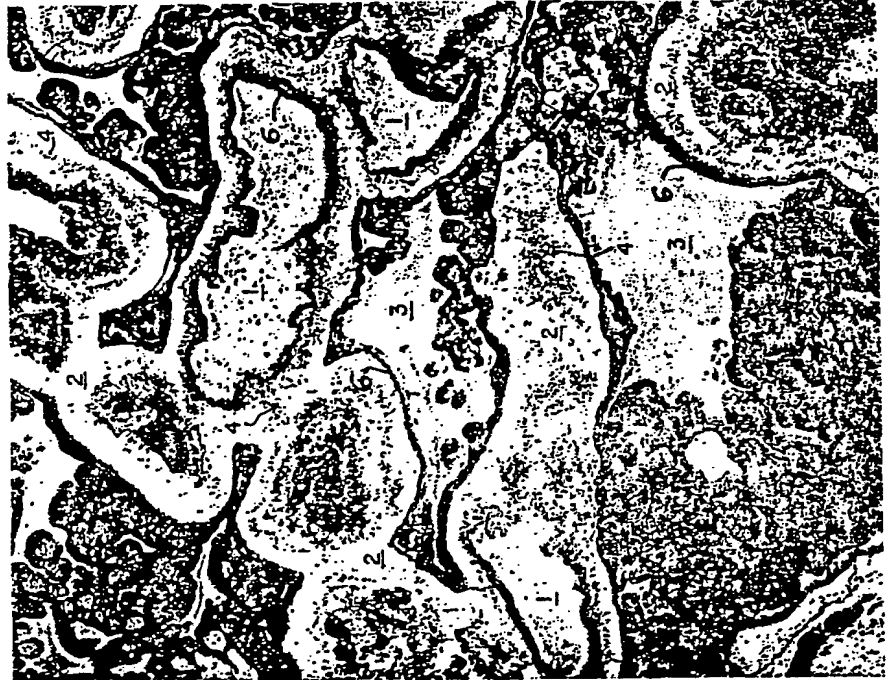


FIG. IV



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FIG.V

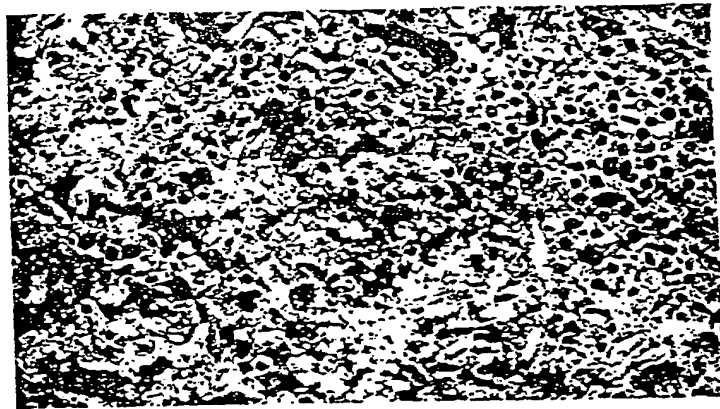
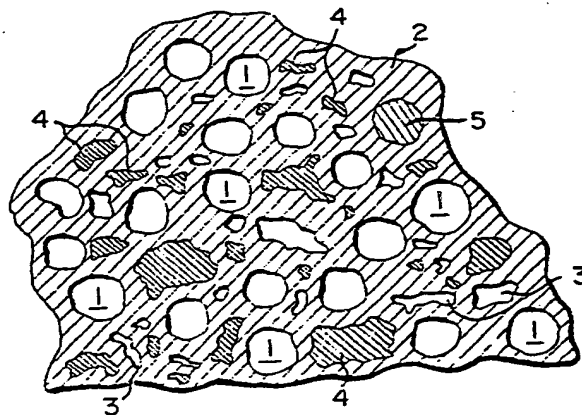


FIG.VI



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COMPLETE SPECIFICATION

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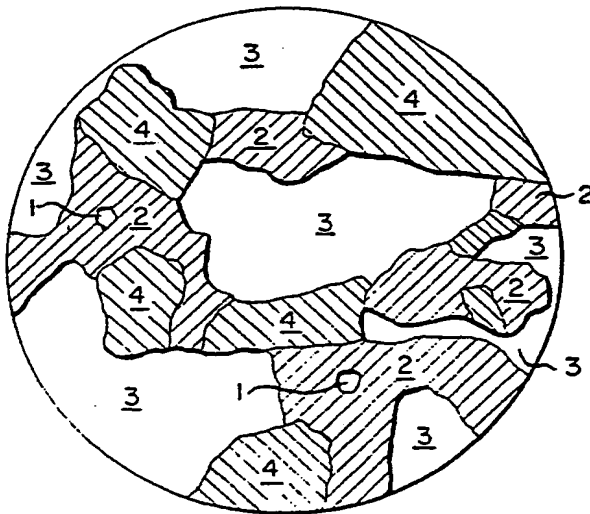
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SHEETS 3 & 4

FIG. VII



FIG. VIII



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SHEETS 3 8 4

FIG. VII



FIG. 7

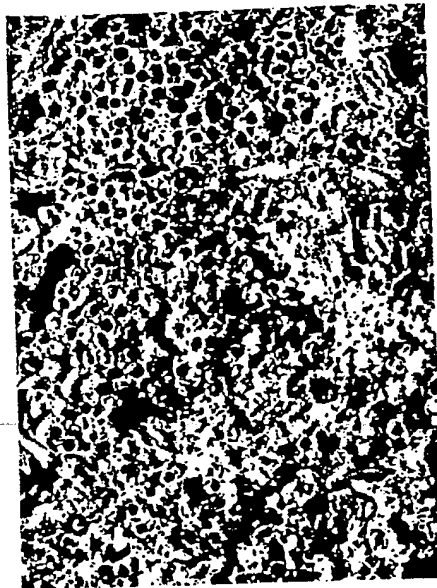


FIG. VIII

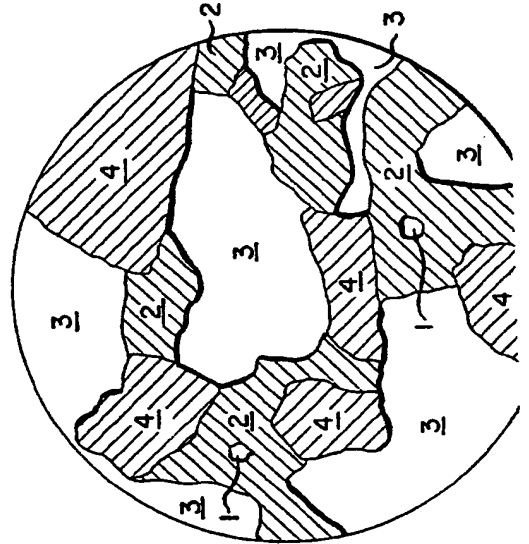


FIG. VI

